

High capacity surface route discharge at the potassium-O₂ electrode

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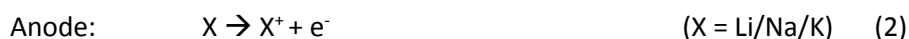
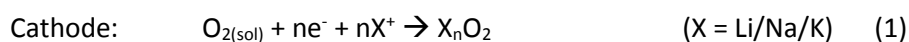
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Abstract

Discharge by a surface route at the cathode of an aprotic metal-O₂ battery typically results in surface passivation by the non-conducting oxide product. This leads to low capacity and early cell death. Here we investigate the cathode discharge reaction in the potassium-O₂ battery and demonstrate that discharge by a surface route is not limited to growth of thin (<10 nm) metal oxide layers. Electrochemical analysis and *in situ* Raman confirmed that the product of the cathode reaction is a combination of KO₂ and K₂O₂, depending on the applied potential. Use of the low donor number solvent, acetonitrile, allows us to directly probe the surface route. Rotating ring-disk electrode, electrochemical quartz crystal microbalance and scanning electron microscope characterisations clearly demonstrate the formation of a thick > 1 μm product layer, far in excess of that possible in the related lithium-O₂ battery. These results demonstrate a high-capacity surface route in a metal-O₂ battery for the first time and the insights revealed here have significant implications for the design of the K-O₂ battery.

Introduction

Aprotic metal-O₂ batteries have been the focus of intense research due their prospective application as a battery system for long-range electric vehicles and other energy demanding applications.[1-6] During the discharge process of a typical aprotic metal-O₂ battery, an alkali metal anode, e.g. Li/Na/K, is oxidised, which produces alkali ions that take part in an oxygen reduction reaction (ORR) at the cathode forming superoxide, peroxide or other oxide species, as shown below.



The Li-O₂ battery is the most promising due to a theoretical specific energy of 3500 Wh kg⁻¹ based on the discharge product Li₂O₂.^[1] The Na-O₂ battery has a specific energy of 1105 Wh kg⁻¹ or 1602 Wh kg⁻¹, based on the formation of NaO₂ and Na₂O₂ on discharge, respectively.^[7] The K-O₂ battery has a specific energy of 935 Wh kg⁻¹ and is believed to form KO₂.^[8] Although the specific energy of the Na-O₂ and K-O₂ batteries are notably lower than that of the Li-O₂ battery, both demonstrated much smaller polarisation and significantly higher energy efficiency during discharge and charge. The voltage gap between discharge and charge is ~100 mV for Na-O₂ and ~50 mV for K-O₂, compared to 1 V for Li-O₂.^[8-10] This variation is attributed to the different type of discharge product, superoxide in Na-O₂/K-O₂ versus peroxide in Li-O₂. Recently the chemistry at the cathode in the aprotic Li-O₂ battery has been

established and two competitive routes have been demonstrated on discharge, the solution route and the surface route.[11, 12] The former results in growth of Li_2O_2 as a chemical step from solution, leading to a high capacity and rate capability, while the latter forms a Li_2O_2 film on the electrode surface, resulting in low rates and capacities. Similar mechanisms are known to occur in other aprotic metal- O_2 batteries.[13, 14]

When discharging a metal- O_2 battery by a surface route, conductivity of the newly formed phase is critical. However, the importance and origin of conductivity in metal- O_2 batteries remains under debate. Curtiss and Amine *et al* have proposed that Li_2O_2 deposits have a superoxide like character,[15-17] resulting in a quasi-semiconductor like material. Siegel *et al* have suggested conductivity within the bulk by formation of hole and electron polarons and defects in the form of site vacancies.[18, 19] In practice, the Li_2O_2 film formed on discharge is restricted to a thickness of 7 nm due to its low electric conductivity, 10^{-12} - 10^{-11} S cm^{-1} at 100 °C.[20, 21] As a result, surface route discharge in the Li- O_2 battery typically results in a low capacity and premature cell death and therefore the solution route is overwhelmingly desired.[1] In addition, similar studies of the Na- O_2 system also suggest that conductivity of NaO_2 is limited and that discharge by a surface route is not a dominant discharge pathway,[14, 22] although calculation shows that NaO_2 has a higher conductivity than LiO_2 . [23]

Since the K- O_2 battery was reported in 2013,[8] only a few studies of the system have been reported and the discharge mechanism in the K- O_2 battery remains poorly understood.[24-27] Here we explore discharge in the K- O_2 battery using solvents that are expected to induce a surface route. We show that capacity, far in excess of that for a thin film, can be passed during discharge by a surface route in the K- O_2 battery. We confirm an electrodeposition route by rotating ring-disk electrode (RRDE) and electrochemical quartz crystal microbalance (EQCM) methods and characterise the discharge product using *in-situ* surface-enhanced Raman spectroscopy (SERS). We highlight that this is the first report of a surface route discharge mechanism in aprotic metal- O_2 chemistry, able to form a thick, high capacity, surface layer. Finally, we propose some possible origins of this effect and consider the implications for the K- O_2 battery.

Results and discussions

Figure 1a shows cyclic voltammograms (CVs) for dioxygen reduction in presence of K^+ and Li^+ in CH_3CN . CH_3CN was selected as the solvent as it is known to favour a surface-confined reaction rather than a solution reaction with dissolved intermediates, while also possessing high conductivity and limited Raman peaks. While both CVs are similar in shape, it is immediately evident that the peak current and charge passed in the K- O_2 system far exceed that of the Li- O_2 system. It is also worth noting that the ratio of charge passed on oxidation over charge passed on reduction is far higher in the K- O_2 system, 0.90, than that in the Li- O_2 system, 0.18. This high ratio suggests that the reduction product in the K- O_2 system can be easily oxidized, unlike the Li- O_2 system, and implies a high degree of chemical reversibility. As discussed above, oxygen reduction to form alkali oxides in CH_3CN (low donor number, DN) is known to form insulating solids at the electrode surface resulting in low currents and low charge passed. The fact that the K- O_2 system does not fit into this theory is intriguing and to date unexplored. We highlight that similar CVs are published in the literature but their significance has not been realised.[8]

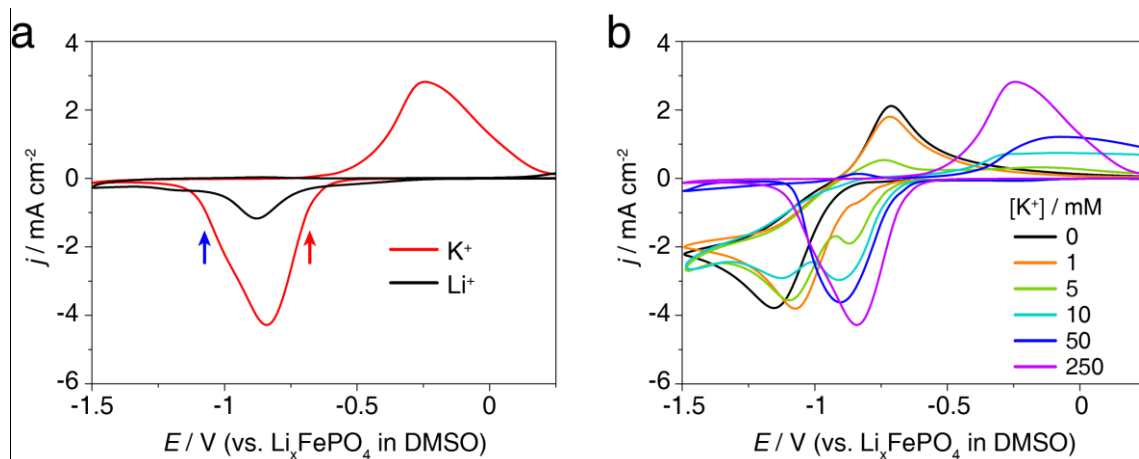
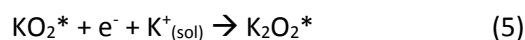


Figure 1. Cyclic voltammetry (CV) of dioxygen in the presence of K^+ and Li^+ ions in CH_3CN . (a) Comparison of the voltammetric response with 250 mM Li^+ or K^+ ions only. Arrows indicate the potentials at which SERS spectra were recorded. (b) Voltammograms recorded with increasing K^+ concentration where the total salt concentration is maintained at 250 mM using a tetrabutylammonium, TBA^+ , salt. Measurements were performed in O_2 saturated solutions with 250 mM of the relevant triflate salt at a Au electrode at 100 mV s^{-1} .

Dioxygen reduction in $K-O_2$

CVs for the ORR in CH_3CN with varying K^+ amounts are shown in **Figures 1b**. With TBA^+ ions only, the well-known quasi-reversible redox couple O_2/O_2^- is observed, equation 3.[28, 29] Upon addition of K^+ ions in place of TBA^+ , a new peak occurs at positive potentials and this shifts positive in potential and increases in magnitude as the concentration of the alkali ion is increased. The new peak has characteristics consistent with formation of an insulating product (peak followed by a drop to near zero current) and the formation is at the expense of the original reduction peak. The positive shift of the onset potential is consistent with stabilisation of the superoxide by the K^+ ion, similar to that proposed in other metal- O_2 systems, equation 4.[13, 30]



Unlike $Li-O_2$, disproportionation of KO_2 can be ruled out on the grounds of thermodynamics ($\Delta G_{f,KO_2} < \Delta G_{f,K_2O_2}$). A calculation of the free energy change can be found in the Supplementary Information. Close inspection of the reduction peak for $K-O_2$, **Figure 1a**, shows that it consists of two peaks, with one at higher and one at lower potentials, where the latter is a shoulder on the negative side of the former. We note that this second lower potential reduction peak is not due to the original O_2/TBA redox couple as no TBA^+ is present in the Fig 1a and an analysis of soluble O_2^- discussed later does not show any coloration of this peak with a solution phase O_2^- . It is well established in the $Li-O_2$ field that LiO_2 can be reduced to the peroxide and this peak suggests a similar process is occurring in $K-O_2$, where KO_2 is further reduced to K_2O_2 , equation 5. Indeed, electrochemical reduction of KO_2 is likely to occur in all systems at some potential.[6, 31] These data suggest that the two peaks are due to the formation of KO_2 and K_2O_2 . To confirm this, *in situ* SERS was recorded while holding the potential at a high voltage, -0.7 V (vs. Li_xFePO_4 in DMSO) and a low voltage, -1.1 V (vs. Li_xFePO_4 in DMSO), where we expect to

form mainly superoxide and peroxide, respectively (**Figure 2**). A table showing the assignment of all peaks in the spectra and a table of standard Raman peak positions for common compounds in the K-O₂ battery are provided in the Supplementary Information. When holding the potential at -0.7 V, a new peak occurred at 1132 cm⁻¹ consistent with the formation of KO₂, i.e. a blue shift from the free O₂⁻ position (1108 cm⁻¹) towards the bulk crystal KO₂ position (1145 cm⁻¹). When stepping the potential to -1.1 V, the peak for KO₂ disappeared and a new peak occurred at 816.3 cm⁻¹, which is in the region we expect to see a peroxide O-O stretch, indicating that this peak is due to formation of K₂O₂.

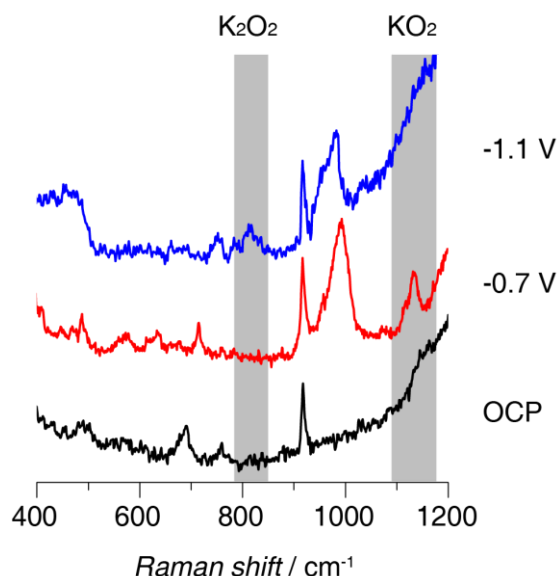


Figure 2. Showing *in situ* SERS during ORR with K⁺ in CH₃CN. Spectra collected at a Au electrode during O₂ reduction in the presence of 250 mM KTFA at -0.7 V and -1.1 V (vs. Li_xFePO₄ in DMSO), as indicated by the matching coloured markers in the CVs, **Figure 1a**. (Black) open circuit potential. Shaded region shows the position of the superoxide and peroxide peaks.

While interesting, the results thus far cannot explain why significantly more charge is passed in K-O₂ in comparison to Li-O₂. The charge passed in the K-O₂ system far exceeds that expected for an electrodeposited thin film based on the conductivity of either KO₂ or K₂O₂ although a passivating limit is evident.[32] This indicates conductivity or partial solubility. However, both KO₂ and alkali peroxides are considered insulating, although debate exists in the literature regarding the conductivity of KO₂, and both have little or no solubility in this solvent.[20, 32, 33] We note that the effect can also be observed in other solvents such as dimethyl sulfoxide (DMSO) and diethylene glycol dimethyl ether (diglyme), **Figure S3**. By holding at a low potential to drive reduction of O₂ to K₂O₂, very similar amounts of capacity were consumed to form the surface film, suggesting the products in three solvents had very similar conductivities. Here we only use these solvents as a means of testing our proposed theory. Ether based electrolytes are currently used in K-O₂ cells,[8] but DMSO is not a viable solvent for a practical battery and is unstable against metallic K.

Solution versus surface routes

In the following section we explore the solubility of reaction intermediates by RRDE voltammetry and the growth of surface products by EQCM for K-O₂. In tandem, these two techniques provide a unique ability to observe both solution and surface routes in metal-O₂ systems.

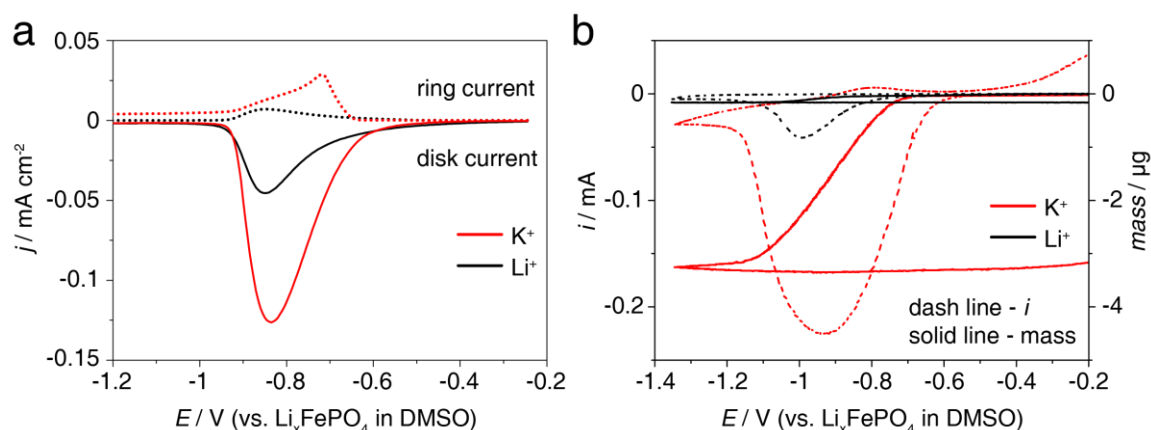


Figure 3. RRDE and EQCM measurements of O_2 reduction showing significant surface route discharge with K^+ in comparison to Li^+ containing electrolytes. (a) Polarization curves obtained in O_2 saturated CH_3CN containing 250 mM LiTFA (black) or KTFA (red). The RRDE was a 5 mm diameter Au disk with a Au ring and the rotation rate was 2000 RPM. (b) Cyclic voltammetry of oxygen reduction with 250 mM LiTFA (black) and KTFA (red) in CH_3CN (dashed lines) and EQCM response (solid lines). Measurements were recorded at gold coated quartz crystals at 20 mV s^{-1} .

The RRDE results, **Figure 3a**, are similar to the static voltammograms, and are consistent with the surface dominant reaction expected in CH_3CN . The ring current indicates the amount of soluble superoxide in the system and as previously shown,[11] this is limited in $Li-O_2$. The data shows that the solubility of KO_2 in CH_3CN is also low and at this level it cannot explain the large charge passed during reduction, *i.e.*, the product of the reduction is not simply dissolving into solution and avoiding surface passivation. This demonstrates that solubility cannot explain the increased charge associated with $K-O_2$. **Figure 3b** shows EQCM results for $Li-O_2$ and $K-O_2$, respectively, and both show an increase in mass roughly proportional to the charge passed. This confirms the formation of a surface film on reduction, rather than formation of soluble products, which is consistent with RRDE results. Most significantly, more mass is electrodeposited in $K-O_2$ in comparison to $Li-O_2$. This unequivocally demonstrates that the increased charge passed in the $K-O_2$ system results in the formation of a thick film of product on the electrode surface and that this forms by a surface route, which is unique in the field of aprotic metal- O_2 . Due to the mixed product and small solubility of KO_2 we cannot confirm the nature of the product from the EQCM data, *i.e.*, by relating $\Delta\text{mass}/\Delta\text{charge}$.

Figure 4 shows scanning electron microscopy (SEM) images of the discharge product formed during dioxygen reduction in $K-O_2$ at a Au wire. Notably, the product film formed appears continuous and free from holes, **Figure 4a**, consistent with an electrochemical growth. **Figure 4b** shows an etched cross-section at the Au wire, which shows a thick deposit on the electrode surface. **Figure 4c** shows a section of the film, which has delaminated from the underlying electrode during drying and unmistakably demonstrates the thickness of the film formed. Raman and FTIR characterisation of this film are shown in **Figure S4**, and these show that the film mainly consists of KO_2 . We do not expect to see K_2O_2 *ex situ* as this will likely decompose to KO_2 in the O_2 atmosphere of the cell (see discussion in the Supplementary Information).

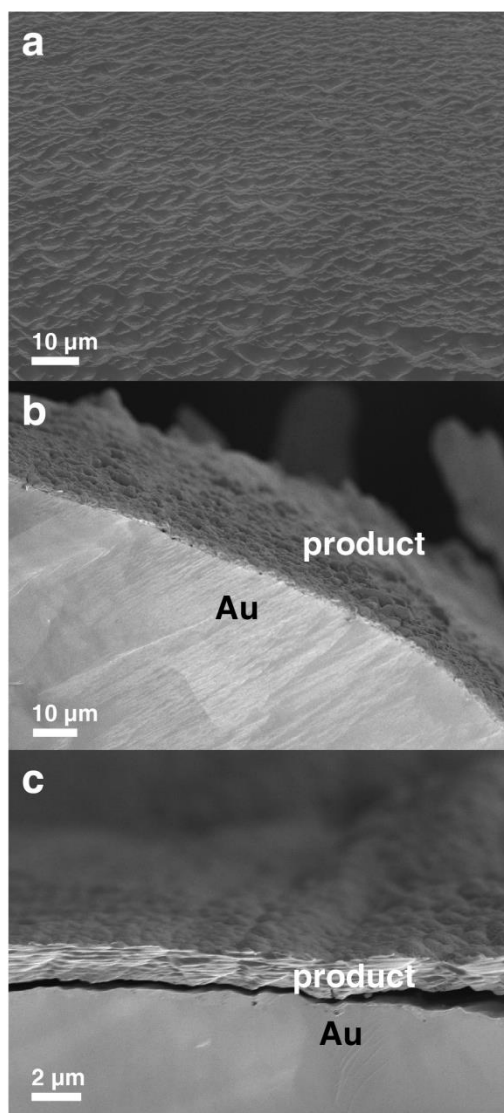


Figure 4. Morphology of the discharge product of the K-O₂ reaction at a Au wire electrode. SEM images showing (a) the surface of and (b, c) cross sections of the resulting discharge product formed on a Au wire. The Au wire was discharged at -1.1 V (vs. Li_xFePO₄ in DMSO) in O₂ saturated 250 mM KTFA in CH₃CN in a 3-electrode glass cell.

To further explore the growth mechanism of the superoxide-like product in K-O₂, electrochemical impedance spectra were recorded during discharge at a planer Au electrode, **Figure 5** and **Figure S5**. In all systems at the earlier stages of discharge we observed a single semi-circle in the Nyquist plot with a tail at lower frequencies. This is a typical EIS response of the positive electrode charge transfer reaction in metal-O₂ batteries.[34] The resistance, *R*, of the single semi-circle is associated with the charge transfer reaction and therefore, conductivity of the surface film. Considering first the Li-O₂ system, while *R* is initially low, this rapidly increases after only 2.5 mC cm⁻² of charge (c.a. 35 s), **Figure S6**, and is accompanied by a large voltage polarisation in the D.C. measurement. In contrast, for the same amount of charge passed, *R* does not change significantly in the K-O₂ system.

R steadily increases during discharge from c.a. 10 kOhm to 18 kOhm during the first 175 s of discharge, indicating the potassium oxide film formed introduces a gradually increasing resistance to charge transfer, but not to a point of complete passivation. As the discharge approaches completion the EIS spectrum does not show a clear RC response for an electron transfer, indicating that the conductivity is now insufficient to maintain the discharge, i.e., the thick potassium oxide film has now passivated the surface. This happens at a capacity of c.a. 10 mC cm⁻² of charge, and may be due to passivation by KO₂ and K₂O₂ or some products from side-reactions, which will preferentially form at negative potentials. These data, in conjunction with the ECQM data demonstrate that in the K-O₂ system, the discharge product formed by a surface route displays enhanced conductivity compared to other alkali ion metal-O₂ discharge products and forms by a classical electrodeposition mechanism.

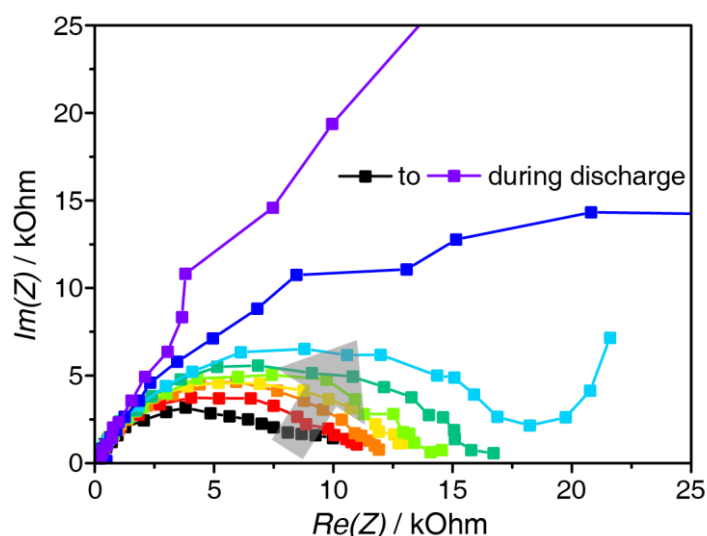


Figure 5. Nyquist plot showing the limited increase in charge transfer resistance during K-O₂ discharge. Measurements were performed at 50 $\mu\text{A cm}^{-2}$ in O₂-saturated 250 mM KTFA CH₃CN at a planar Au electrode. The load curve for the discharge is shown in **Figure S5** in the SI.

Rationalising conductivity in K-O₂

Our results strongly suggest the presence of a conducting phase during discharge in K-O₂ and as mentioned, this has been shown, if not discussed previously.[8] However, this increasing conductivity is intriguing. One possibility is significant side-reaction with the solvent. But we note that K-O₂ does not readily react with CH₃CN and that we observe a similar effect in other solvents, making this an unlikely scenario. A study of the conductivity of alkali oxides showed them to be effectivity insulating, which fails to explain the effects observed here.[22] However, we note that conflicting reports exist for the conductivity of KO₂, which has been described as a room temperature semiconductor, whereas other reports suggest a room temperature conductivity of 10⁻¹³ S cm⁻¹. [32, 35] It has been proposed that one of the primary factors controlling conductivity in these oxides is the ability of the dioxygen to take varying oxidation states, i.e., O₂²⁻, O₂¹⁻, O₂⁰, the relative formation energy of such sites and consequently their concentration.[18] Their occurrence within the peroxide or superoxide lattice provides routes to both hole polarons and electron polarons (charged polarisation within the lattice).[22] For example, a superoxide like dioxygen in a peroxide lattice effectivity creates a hole due to the missing electron. Conversely, inclusion of a peroxide in a superoxide lattice forms an electron conductor. As KO₂ is more stable than K₂O₂, see Supplementary Information, retaining superoxide like character in the oxide layer may be favourable resulting in the formation of a mixed product (various

oxygen valences) and consequently, increasing concentration of polaron charge carriers. Finally, it should be noted that we cannot rule out conductivity in non-crystalline phases, such as amorphous oxides and grain boundaries.

CONCLUSION

Here we show for the first time that in an aprotic metal-O₂ battery system, a large discharge capacity can be obtained from a surface discharge route. While the origin of this effect remains elusive, the implications are significant, as a new class of metal-O₂ battery could be realised where the challenge of obtaining a high capacity is entirely different from that in the Li-O₂ and Na-O₂ systems. While the latter rely on partial solubility or redox mediators to promote large capacities and high rates, these appear implicit in the chemistry of the K-O₂ battery cathode reaction. These insights should be carefully considered in the design and performance of K-O₂ cells.

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NOTES

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